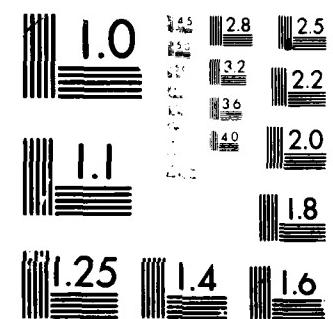


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SHOCK TUBE STUDIES OF THE N₂O/CH₄/CO/Ar AND N₂O/C₂H₆/CO/Ar SYSTEMS

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Technical Report UMO-5-PU

PROJECT SQUID

A COOPERATIVE PROGRAM OF FUNDAMENTAL RESEARCH
AS RELATED TO JET PROPULSION
OFFICE OF NAVAL RESEARCH, DEPARTMENT OF THE NAVY

CONTRACT N00014-75-C-1143 NR-098-038

SHOCK TUBE STUDIES OF THE $N_2O/CH_4/CO/Ar$
AND $N_2O/C_2H_6/CO/Ar$ SYSTEMS

by

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April 1979

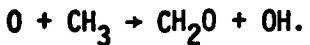
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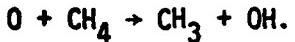
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ABSTRACT

Reflected shock waves were used to heat $N_2O/C_2H_6/CO/Ar$ and $N_2O/CH_4/CO/Ar$ mixtures to temperatures of 1875-2855 K at total concentrations of $5 \times 10^{18} \text{ cm}^{-3}$. Oxygen atom production was monitored via the flame band emission at 450 nm, and CO_2 production was observed at 4.27 μm . These data were then compared to the results of numerical integration of the rate equations, using rate constant and mechanistic information obtained in earlier studies of H_2 and CH_2O oxidation under similar conditions. For the C_2H_6 mixture, it was possible to achieve good agreement between these calculations and the observed data using only one additional reaction

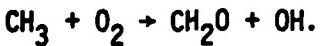


The calculations were insensitive to the precise value used, but the results are consistent with recent high temperature literature values. For the CH_4 mixture, the best agreement was achieved using a recent high temperature value for



The data indicated that this reaction has a markedly non-Arrhenius rate constant; use of a value based upon low temperature data gives results inconsistent with those observed. The CH_4 system was insensitive to any other methane reaction rate constant. There was some experimental evidence to suggest an unsuspected complexity in methyl radical decay channels at the lowest temperatures observed.

The mechanism/rate constant combination used here was then applied to the analysis of literature data for CH_3 oxidation by O_2 . This analysis was designed to obtain a value for the rate constant of



Results indicated that the most recent high temperature studies yield values consistent with the present analysis.

INTRODUCTION

This paper presents the results of the next step in our study of kinetically simplified oxidation systems [1,2]. In an attempt to more accurately characterize certain high temperature rate constants, we have studied systems where oxygen atoms were produced at well defined rates via N_2O dissociation; the oxygen atom profile was then followed as the atoms reacted with added fuel molecules. In principle such an approach should yield reliable rate constant information for the reaction between oxygen atoms and the fuel molecule of interest. In practice such an assignment can be quite difficult due to the inevitable presence of competing reactions of various types. To attempt to circumvent this problem, this approach was first applied to the well-characterized H_2 system [1]. Although it might appear that the next step would be to study methane, it soon became apparent that additional information was required on the reactions of formaldehyde. The recent completion of such a study [2] suggested this system was sufficiently well characterized to proceed to a more complex system.

Prior to study of the practically important CH_4 system, it was thought prudent to study a system involving methyl radicals. The first phase of the present study focused upon reactions of methyl radicals produced via very rapid dissociation of ethane. This approach is analogous to that used earlier [3,4] to study the CH_3/O_2 system. The added advantage of the C_2H_6/N_2O system is that one need not account for reactions of O_2 and thus the analysis is more straightforward, particularly in light of the earlier work on H_2 and CH_2O under similar conditions.

The results of this analysis were then in hand when the N_2O/CH_4 data were analyzed. Here the prime purpose was to see if the results obtained were consistent with the recent work [5,6] which indicated that the rate constants for

the reactions of O and OH with CH_4 had a non-Arrhenius temperature dependence. Such information is particularly important with respect to the proper choice of rate constants for use in modeling studies of combustion processes.

The results described herein suggest that it is possible in most instances to obtain very good agreement between calculated and observed profiles using the "best" literature values for the pertinent rate constants. However there is some evidence to suggest that there may be an additional methyl radical decay route at the lowest temperatures studied. These results were then extended to include an analysis of the CH_3/O_2 system with particular emphasis upon assignment of a high temperature rate constant for the reaction between methyl radicals and molecular oxygen. This analysis indicated that the best choice here was consistent with that recently obtained from studies of more complex systems.

EXPERIMENTAL

The 7.6 cm shock tube, gas handling system, and optical configuration have been described previously [7]. Infrared emissions were collimated by two slits 1.5 mm wide and 5 mm high placed 50 mm apart. After passing through a filter, the emissions were focused upon a liquid-nitrogen-cooled indium antimonide detector; the detector-preamp combination had a nominal rise time of 1 μ s. CO_2 was monitored with a 4.27 μm interference filter (FWHM = 0.18 μm). The flame-band emissions were monitored by a RCA 1P28A/V1 photomultiplier mounted behind a 450 nm interference filter (FWHM = 6.5 nm) and two slits 1 mm wide by 2 mm high which were 38 mm apart. The measured response time of the photomultiplier/preamp system was less than 2 μ s. Data were collected with either a Biomation Model 805 transient recorder or the system previously described [8]. Biomation data were collected at 0.5 μ s intervals while the other device collected data at 10.0 μ s intervals.

Gases used were AIRCO Ar (99.9995%) and N_2O (99.995%), Matheson CO (99.99%), C_2H_6 (99.96%) and CH_4 (99.99%). The CO was slowly passed through a coil of copper tubing at 77K before addition to the vacuum line. Other gases were used as supplied.

The shock tube was pumped down to \sim 2 mPa and the observed leak-outgassing rate was usually near 2 mPa/min. The tube was isolated from the pumps for approximately one minute prior to shock initiation; the nominal background pressure was near 4 mPa. Since the test section was pressurized to 2.7 kPa with the mixtures of interest, the background impurities for the shock tube were present in the low ppm range in the shocked mixtures. Mylar diaphragms and helium driver gas were used throughout.

Temperatures behind the reflected shocks were computed in the usual way from measured incident shock velocities. Reflected shock pressures were measured with a fast response pressure transducer and were always found to be in good agreement with those calculated. Furthermore, the reflected shock pressure was always constant over the time interval that data were collected; as a result, no attempt was made to correct for non-ideal effects.

RESULTS

Flame-band Signal

Information about oxygen atom production was obtained by observing the flame-band emissions at 450 nm in systems containing added CO. The procedure is completely analogous to that used previously [1]. Mixtures studied are listed in Table 1. As in the earlier work, additional mixtures were prepared which were similar to those listed except that CO was omitted. Here the time-resolved emissions at 450 nm were recorded and used as background for the experiments of interest. The calibration factor relating the flame-band intensity to the product of the CO and O concentrations was the same as that used earlier. Additional checks of this factor during the course of these experiments verified the value. Data were collected at 0.5 μ s intervals. For convenience in the data reduction process, times were measured relative to t_0 , the time at which the reflected shock was calculated to be first visible at the detector. This point was determined by simple geometrical optics arguments using the collimating slit dimensions employed for these experiments. Typically t_0 is $\sim 5 \mu$ s earlier than t_{mp} , the time of shock passage of the window midpoint.

The results of typical experiments are shown in Fig. 1. Here three parameters were used to characterize the signal. The first, $t_{1/2}$, designates the time, relative to t_0 , when the signal reaches one-half its maximum value. Similarly, $t_{3/4}$ is the time when the signal reaches three-fourths the maximum. V_m specifies the maximum signal observed. Three factors were explicitly considered in an error analysis of these data: (1) Measurement errors, including noise, calibration errors, and errors in background corrections, (2) errors of $\pm 2 \mu$ s in location of t_0 , and (3) errors resulting from temperature uncertainties. More

explicit details of the procedures used in (2) and (3) can be found in Ref. 2. These errors were combined in the standard way [9] to estimate the overall uncertainty. These parameters are shown in Figs. 2 and 3 and listed in Table 1. Note that the scatter observed appears to be consistent with the estimated error bars. These parameters appear to adequately characterize the formation of oxygen atoms in these systems. Although the $t_{1/2}$ values are comparable in Mixtures A and B, there seem to be small but real differences in $t_{3/4}$ and V_m ; the oxygen atoms appear to increase somewhat more slowly in the C_2H_6 mixture and ultimately achieve a higher steady state concentration.

CO₂ Production

Infrared emission at 4.27 μm was observed at 10.0 μs intervals. Here times were measured relative to the passage of the window midpoint by the reflected shock (t_{mp}). Use of this procedure simplified comparisons of calculations and observations. The slower sampling rate here minimized perturbations due to the finite window width.

The observed signal was corrected for emissions from N₂O and CO using procedures described previously [2]. Typical data are shown in Fig. 4. Three parameters were used to characterize these profiles: $t_{0.5}$ indicates the time (relative to t_{mp}) that $[CO_2] = 5 \times 10^{15}/\text{cm}^3$; this was considered to be the lowest concentration at which reliable data could be obtained. $t_{1.5}$ and $t_{2.5}$ indicate the times $[CO_2] = 1.5 \times 10^{16}/\text{cm}^3$ and $2.5 \times 10^{15}/\text{cm}^3$, respectively. The error analysis procedure used here was similar to that used for the flame-band data. In some cases very large error bars result from the fact that, after the "knee" in the profile, small concentration errors result in large time errors. Plots of these parameters are shown in Figs. 5 and 6; they are listed in Table 1. Again it is

seen that the observed scatter is consistent with the calculated error bars. Note that the CO₂ parameters for both mixtures are similar. The minimum seen in the Figs. 5(c) and 6(c) results from diminished CO₂ production at the highest temperatures. For example, the concentration of CO₂ observed at 500 μ s decreases from $\sim 4 \times 10^{16}/\text{cm}^3$ near 2000 K to less than $3 \times 10^{16}/\text{cm}^3$ at 2800 K.

DISCUSSION

As outlined in the Introduction, the thrust of this program has been to attempt to analyze relatively simple kinetic systems of importance in combustion. The emphasis has been to minimize the kinetic ambiguity by proceeding very slowly toward systems of increasing complexity. In this manner, the number of potential variables is reduced to the point where a meaningful analysis should be possible. In practice, this has been achieved by utilizing all of the information from past work as fixed quantities not subject to modification in an attempt to fit the new data. Of course, some modifications may ultimately be required, e.g., the change in the rate constant assignment for $H + N_2O = N_2 + OH$ [1,2], but this approach serves to provide a much more constrained system in which fortuitous agreement of observations and calculations would appear to be more unlikely.

The likely mechanism for the $N_2O/C_2H_6/CO/Ar$ system (Mixture A) (assuming sufficiently rapid C_2H_6 dissociation) is listed in Table 2 as Reactions 1-19. The most important feature of this mechanism is that, in spite of its apparent complexity, information is available about eighteen of these reactions from studies of simpler systems with the same experimental apparatus used in this work. Given the fact that good agreement between experiments and calculations were achieved there, one can consider the present analysis to consist of simply analyzing the effect of the one additional reaction, namely that between oxygen atoms and methyl radicals (Reaction 5).

In the calculations with this mechanism, provisions were made for both the finite observation window width and detector response times as in the earlier work [2]. The flame-band calculations included the calibration factor so that the computed output was in effect an absolute oxygen atom concentration-time profile;

no normalization factors were used. The slit corrected flame-band output could then be directly compared to the observations with t_0 as the reference time. For CO_2 comparisons, slit effects were ignored since data were obtained at 10.0 μs intervals. Here t_{mp} was the reference time, and again it was possible to directly compare calculated and observed profiles using the experimental CO_2 calibration experiments [1,2].

Comparisons were done at selected temperatures. In most cases the experimental parameters were taken directly from Table 1; in a few instances the values were adjusted slightly to better conform to other data in that temperature range. In cases where adjustments were made, the magnitude of the shift was always smaller than the estimated error bar. These representative experimental parameters for Mixture A, with the estimated errors, are listed in Table 3.

The calculated profiles were treated identically to the experimental ones to obtain calculated values of the reaction parameters. The mechanism and rate constants listed in Table 2 [Reactions (1)-(19)] were designated Set 1 and the results are listed in Table 3. These results are also illustrated in Figs. 2 and 5, and the total profile is shown in Fig. 1(a) and 4(a). The agreement seen here is quite reasonable. The possible problem areas include calculated $t_{1/2}$ values which are somewhat long, a calculated temperature dependence of V_m somewhat higher than observed, and a tendency for CO_2 production to be a little slow at long times. However, these problems are quite minor in light of the diverse data, and the fact that the comparisons are made on an absolute concentration-time basis. Particularly encouraging was the fact that no adjustments of any rate constants assigned in the earlier work [1,2] were needed to achieve this fit.

The justification for the assumption that C_2H_6 dissociation is sufficiently rapid so that its precise rate was unimportant was checked in a series of calculations

using 20 reactions. Here C_2H_6 dissociation was included using a rate constant equal to one-half that recently reported by Olson, et al. [22]. (The lower value was used to provide a more rigorous test of the assumption.) This calculation produced results virtually identical to those obtained in Set 1.

The sensitivity of the results to variations in k_5 were checked in Sets 2 and 3 where the rate constant was varied both directions by a factor of two. Note the results are surprisingly insensitive to this variation. These experiments are not capable of providing a more reliable high temperature estimate of this rate constant. It would appear that the best value would be in the range $k_5 = 1-2 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$. This value is consistent with those frequently used at high temperatures [11,14] as well as the recent low temperature measurements [23,24].

Attempts were then made to see if the remaining disagreements between calculations and observations could be related to other reactions of CH_3 . This was checked by additional calculations using a 23 reaction mechanism in which the following reactions were included:



The rate constants for these reactions were taken from Olson and Gardiner [25]. The results are listed as Set 4 in Table 3. Again, there are only marginal differences in the calculated parameters, suggesting these reactions are of little consequence under these conditions. The slightly slower CO_2 production seen here

is probably due to the fact that some of the CH_3 is converted to CH_2 which is "unreactive" in this mechanism and serves as a sink for hydrogen atoms.

In spite of the inability of the present analysis to more precisely determine k_5 , the overall agreement here presents encouraging evidence that the earlier analyses of the H_2 and CH_2O systems [1,2] were reasonable. In retrospect, this system simply provides a method for rapid generation of CH_2O via Reaction (5). This alternative method of generating CH_2O suggests that the formaldehyde concentration in the earlier work was indeed in the expected ranges and there were no significant adsorption problems there.

Calculations with Mixture B were initiated using all of the reactions shown in Table 2. It is important to note that the four reactions involving CH_4 all have rate constants which reflect the recent high temperature data available on these systems. The three radical reactions with methane have rate constants well above a simple Arrhenius extrapolation of low temperature data. The results with this mechanism/rate constant combination are shown in Table 4 (Set I) as well as in Figs. 3 and 6. A representative total profile calculation is shown in Fig. 1(b) and 4(b). In most cases, it can be seen that there is excellent agreement between calculated and observed results. The one real problem concerns $t_{3/4}$ at 2085K. Here the calculation shows a distinct "hitch" just after $t_{1/2}$ where there is a dramatic decrease in the rate of O-atom production for a short time. There is no evidence for such behavior in the observed profiles. However, it must be remembered that the flame-band data were corrected for background emissions and it is possible, but unlikely, that the discrepancy reflects an artifact produced during the data reduction process.

Calculations in which k_{21} , k_{22} , and k_{23} were varied by factors of two each direction indicated the profiles are not sensitive to these rate constants. The

effect of varying k_{20} is shown in Sets II and III. Increases in k_{20} (Set II) cause obvious difficulties with the $t_{1/2}$ flame-band data while slightly improving the CO_2 results. Decreases in k_{20} (Set III) have a mixed effect on the flame-band data while causing CO_2 production to be slower than observed. It would appear that the Roth-Just value used in Set I is probably a reasonable compromise here. Set IV illustrates the effect of using a k_{20} value based upon low temperature flow system data [26]. Although the $t_{1/2}$ and $t_{3/4}$ values at 2085K appear to be a distinct improvement, the complete profile exhibits a significant dip just beyond $t_{3/4}$ which is incompatible with the experimental observations. Furthermore note that there is uniform disagreement here with the CO_2 data. It would appear the present data require a k_{20} value well above what one would expect from the low temperature flow work.

The $t_{3/4}$ discrepancy at 2085K suggests there may be some defects in the mechanism/rate constant combination used here. Detailed analysis of the low temperature results on Mixtures A and B revealed that both calculations showed the hitch in the flame-band production. The usual integration precautions (i.e., decreasing step size, etc.) indicated the problem was not a computational artifact. Instead it resulted from the peaking of the oxygen atom decay rate due to the $\text{O} + \text{CH}_3$ reaction. This phenomenon, coupled with an essentially constant oxygen atom production rate, causes the net production rate to pass through a distinct minima. The problem was not obvious in analysis of Mixture A since the hitch occurred at times well before $t_{1/2}$ there. However, the fact that CH_3 is produced at later times in Mixture B cause this hitch to be more obvious. (Note in Set IV that a lower k_{20} value further delays and exacerbates this feature.)

Assuming that the flame-band data is correct, this discrepancy between ob-

servations and calculations suggests that there may be an alternate CH_3 decay route. Such a route would decrease O-atom decay via $\text{O} + \text{CH}_3$ and thus tend to minimize the hitch. Additional methyl reactions were included in another calculation (Set V) to see if any effects were observed. Here Reactions (24)-(27) were included with the rate constants quoted by Olson and Gardiner [25]. Note in Table 4 that these adjustments did not improve the calculated parameters. It would appear that some other methyl radical reaction must be responsible, but it is not clear at this time what reaction(s) could account for this discrepancy. Note that the presence of an alternate decay mechanism for methyl radicals would also improve the agreement in the $t_{1/2}$ measurements in Mixture A. Here suppression of the oxygen atom "hitch" would result in a lower $t_{1/2}$ value, in better agreement with the observations.

It is important to recognize that the present indications of some unexpected complexities in the mechanism of methyl radical decay are based on fragmentary evidence collected at one extreme of the temperature range observed. It is clear that further work is required to resolve the problem posed here. An obvious route for future experimentation would involve direct observation of methyl radicals utilizing the high temperature spectroscopic data recently obtained by Glanzer, et al., [27]. It would appear that the best information could be obtained at the lower temperatures where there is a much better balance between oxygen atom production and decay channels. Given the high activation energy for N_2O dissociation, the production route is sufficiently large at higher temperatures to mask any subtle changes in the decay mechanism.

In spite of the potential difficulty concerning the low temperature methyl decay, it is apparent that the mechanism/rate constant combination given in Table

2 can accurately describe most of the data. In particular, it is apparent that one must assume a non-Arrhenius temperature dependence for the reaction between oxygen atoms and methane to fit the present data. This conclusion is not contingent upon the other methane rate constant assignments since the calculations were insensitive to these values.

It is possible to use the mechanism/rate constant combination developed in the earlier work [1,2] and confirmed by the agreement achieved in the present study to analyze the data of Izod, Kistiakowsky, and Matsuda [3] with particular emphasis upon determination of the rate constant for Reaction (25), a most controversial reaction [28,29]. IKM used azomethane as a precursor of methyl radicals and then studied the oxidation in a CO/O₂ environment quite similar to that used in our CH₂O oxidation study [2]. Thus, analysis of the IKM data can be considered as a straightforward extension of that work with only two additional reactions to consider:



Attention was limited to consideration of the azomethane data; the analysis of the ethane data in [3] would be dependent upon the ethane dissociation rate due to the lower concentration and temperatures in that work.

In addition to the two reactions listed above the calculations included Reactions (6)-(19) of Table 2 and



The results listed in Set A used the rate constants in Table 2, k₂₅ from Olson and Gardiner [25], and k₂₈ from our earlier work [2]. Although IKM also reported

exponential growth rate constants, these are not listed in Table 5 since semi-log plots of the calculated profiles were sufficiently non-linear to make assignments of λ ambiguous. Although data and calculations are listed at 1500K for completeness, no serious attempts were made to interpret this information since so many of the rate constants used were determined at higher temperatures. There were simply too many potential variables to permit a meaningful analysis here.

Of particular interest in the Set A comparisons is the good agreement indicated for t_i at both 1750K and 2150K. Although the fit for α was not as good, it appears to be reasonable.

The sensitivity of these calculations was then checked in a variety of ways. The effect of methyl radical recombination was analyzed by using the recombination rate used by IKM ($k = 1.4 \times 10^{-11} \text{ cm}^{-3} \text{ s}^{-1}$). These results (Set B) showed little effect above 1500K; use of a more recent value [27] which is significantly lower than that used by IKM indicated, as expected, even less of an effect. Variation of $k_5 (\text{O} + \text{CH}_3)$ showed virtually no effect, but substantial changes were seen when $k_{25} (\text{O}_2 + \text{CH}_3)$ was varied. These changes are illustrated by Sets B and C in Table 5. Note t_i is quite sensitive to k_{25} ; a decrease of a factor of two yields values significantly different from those observed. Values somewhat larger than that used by Gardiner might be acceptable; assignment of limits is difficult here since errors are not assigned in the published data. However, it does appear that a value similar to either Olson & Gardiner's [25] or Tabayashi and Bauer's [28] would be appropriate. It is significant that this value is well above the upper limit reported by Baldwin and Golden [29] at 1220K.

The agreement seen in Table 5 is not as impressive as that reported by IKM in their calculations. However, the present fit was achieved with fewer adjustable

parameters and a more complete mechanism. It is interesting to note, however, that the value reported by IKM for k_{25} is quite close to that used here. At 2000K, the present value is only 40% larger. The major difference in the mechanism used in this analysis is the use of all the formaldehyde decay channels rather than just the oxygen atom reaction used by IMK. As a result the rate constant for this reaction is appreciably slower in this work.

Of course, the disclaimer must be added that the k_{25} assignment is contingent upon the proper mechanistic assignment. If there is an alternate methyl decay route, as might be indicated by the low temperature data in Mixtures A and B, it is conceivable that this rate constant assignment could be too high. However, the alternate route in this case must yield CO_2 at a rate comparable to that proposed here to be consistent with the data.

In spite of the remaining ambiguity, it does appear that the present method of assigning k_{25} is more direct than previous attempts since the number of variables was kept to a minimum. However, it is obvious that additional experiments with other diagnostic tools are required to remove the remaining uncertainties in even these "kinetically simplified" systems.

CONCLUSIONS

It has been possible to accurately describe oxygen atom and CO_2 production for the oxidation of CH_3 and CH_4 by N_2O over an extended temperature range. It was not necessary to adjust any rate constants to achieve the observed fit. The CH_4 analysis confirmed the non-Arrhenius character of the reaction $\text{O} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{OH}$. It was also possible, using the set of rate constants which have now been shown to be consistent with a relatively large data base, to analyze some earlier experiments on CH_3 oxidation by O_2 to obtain an estimate of the rate constant for the reaction $\text{CH}_3 + \text{O}_2 \rightarrow \text{CH}_2\text{O} + \text{OH}$. It would appear that this reaction is important in hydrocarbon oxidation, and its rate constant is now known reasonably well. It is noted that some problem areas still exist even in these kinetically simplified systems, and more work is required here before one can confidently proceed to the analysis of the more complicated hydrocarbon oxidation systems.

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($k_{24} = 7.8 \times 10^{-8} \exp(-390 \text{ kJ/RT})$, $k_{25} = 1.2 \times 10^{-12} \exp(-38 \text{ kJ/RT})$,
 $k_{26} = 1.2 \times 10^{-9} \exp(-63 \text{ kJ/RT})$, and $k_{27} = 1.2 \times 10^{-11}$.)
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TABLE 1. SUMMARY OF EXPERIMENTAL OBSERVATIONS

Mixture ^a	T/K	Flame Band				CO_2 Production		
		$\text{N}/10^{18} \text{ cm}^{-3}$ ^b	$t_{1/2}/\mu\text{s}$ ^c	$t_{3/4}/\mu\text{s}$ ^d	v_m ^e	$t_s/\mu\text{s}$ ^f	$t_{1.5}/\mu\text{s}$ ^g	$t_{2.5}/\mu\text{s}$ ^h
A	2020	4.97	28	47	0.36	23	43	65
	2080	5.05	17	35	0.45	19	34	52
	2130	5.11	--	--	0.55	16	31	49
	2305	5.31	9	16	1.06	7	15	28
	2410	5.40	11	19	1.25	8	15	26
1.01% N_2O	2485	5.41	8	17	1.50	--	15	38
12.10% CO	2595	5.52	8	14	1.84	--	13	140
256 ppm C_2H_6	2660	5.57	6	12	2.25	--	--	195
	2720	5.58	6	12	2.21	--	--	235
	2745	5.60	6	11	2.50	--	12	290
	2765	5.64	6	11	2.45	--	--	300
	2770	5.74	8	11	2.40	--	--	290
	2810	5.73	8	11	2.72	--	13	270
	2855	5.76	7	10	2.83	--	14	370

(continued)

TABLE 1. SUMMARY OF EXPERIMENTAL OBSERVATIONS (continued)

Mixture ^a	T/K	$M/10^{18} \text{cm}^{-3}$ ^b	Flame Band			CO_2 Production		
			$t_{1/2}/\mu\text{s}$ ^c	$t_3/t_1/\mu\text{s}$ ^d	V_m^e	$t_s/\mu\text{s}$ ^f	$t_{1.5}/\mu\text{s}$ ^g	$t_{2.5}/\mu\text{s}$ ^h
B	1875	4.81	--	--	--	60	115	160
	2085	5.10	17	25	0.35	22	35	56
1.00% N ₂ O	2090	5.06	15	20	0.37	19	33	50
12.12% CO	2105	5.04	17	22	0.36	20	38	54
503 ppm CH ₄	2180	5.19	19	27	0.60	16	26	38
	2275	5.23	10	13	0.83	--	19	30
	2375	5.36	9	15	1.08	8	16	25
	2435	5.41	10	15	1.20	8	14	26
	2495	5.45	9	12	1.31	9	16	27
	2560	5.53	10	12	1.45	--	14	38
	2615	5.54	8	13	1.65	--	12	80
	2690	5.64	8	11	2.15	--	--	72
	2695	5.58	6	9	2.00	--	--	162
	2715	5.63	6	10	2.30	--	--	152
	2825	5.71	6	10	2.55	7	12	290
	2840	5.72	7	8	2.45	--	--	300

^aBalance was argon.^bTotal concentration.^cTime relative to t_{mp} (see text) when signal is one-half maximum value.^dTime relative to t_{mp} when signal is three-fourths maximum value.^eMaximum signal^fTime relative to t_{mp} (see text) when $[CO_2] = 0.5 \times 10^{16} / \text{cm}^3$.^gTime relative to t_{mp} when $[CO_2] = 1.5 \times 10^{16} / \text{cm}^3$.^hTime relative to t_{mp} when $[CO_2] = 2.5 \times 10^{16} / \text{cm}^3$.

TABLE 2. MECHANISM AND RATE CONSTANTS

<u>Reaction</u>	<u>Rate Constant^a</u>				<u>Reference</u>
	<u>log₁₀ A</u>	<u>n</u>	<u>E_A</u>		
1. N ₂ O + M = N ₂ + O + M	-9.57	0	216		1
2. N ₂ O + O = 2NO	-10.11	0	117		10
3. N ₂ O + O = N ₂ + O ₂	-10.11	0	117		10
4. N ₂ O + H = N ₂ + OH	-8.82	0	92		2
5. O + CH ₃ = CH ₂ O + H	-10.00	0	0		11
6. O + CH ₂ O = HCO + OH	-10.52	0	12.9		12
7. H + CH ₂ O = HCO + H ₂	-9.26	0	44		2
8. OH + CH ₂ O = HCO + H ₂ O	-10.90	0	0.6		13
9. M + CH ₂ O = HCO + H + M	-7.26	0	339		2
10. O + HCO = CO + OH	-9.77	0	0		14
11. H + HCO = CO + H ₂	-9.48	0	0		14
12. OH + HCO = CO + H ₂ O	-9.77	0	0		14
13. M + HCO = CO + H + M	-9.59	0	61.4		15
14. O + CO + M = CO ₂ + M	-33.80	0	0		10
15. OH + CO = CO ₂ + H	-11.18	0	33.4		16
16. O + H ₂ = OH + H	-9.44	0	57.3		17
17. OH + H ₂ = H ₂ O + H	-10.44	0	21.5		18
18. H + O ₂ = OH + O	-6.69	-.91	69.5		19
19. O + H ₂ O = 2OH	-9.96	0	76.9		20
20. O + CH ₄ = CH ₃ + OH	-9.17	0	58.5		5
21. H + CH ₄ = CH ₃ + H ₂	-8.92	0	63.1		21
22. OH + CH ₄ = CH ₃ + H ₂ O	-17.59	2.13	10.2		6
23. M + CH ₄ = CH ₃ + H + M	-6.11	0	390		21

^aExpressed in the form $k = AT^n \exp(-E_A/RT)$ in units of cm³, molecule, sec, and kJ.

TABLE 3. COMPARISON OF CALCULATIONS AND OBSERVATIONS (MIXTURE A)

<u>Parameter^a</u>	<u>T/K</u>	<u>Observed</u>	<u>Set 1^b</u>	<u>Set 2^c</u>	<u>Set 3^d</u>	<u>Set 4^e</u>
Flame band						
$t_{1/2}$	2020	28± 5	36	36	33	34
	2410	9± 2	13	14	--	14
	2855	7± 2	9	9	9	9
$t_{3/4}$	2020	47±13	54	52	55	53
	2410	17± 4	19	19	--	20
	2855	10± 3	11	11	11	11
v_m	2020	0.36±.06	0.29	0.29	0.30	0.30
	2410	1.25±.15	1.28	1.25	--	1.32
	2855	2.83±.32	3.29	3.20	3.38	3.37
CO_2						
$t_{.5}$	2020	23± 4	26	24	28	28
	2410	8± 2	9	8	--	9
	2855	--	5	4	5	5
$t_{1.5}$	2020	43± 5	49	47	51	52
	2410	15± 3	18	17	--	19
	2855	14± 3	11	11	14	13
$t_{2.5}$	2020	65± 6	77	77	80	82
	2410	26± 4	34	33	--	37
	2855	370±80	509	448	560	525

^aSee TABLE 1 for definitions.^bReactions 1-19 (TABLE 2).^cHere $k_5 = 2 \times 10^{-10}$.^dHere $k_5 = 5 \times 10^{-11}$.^eHere included additional CH_3 reactions (see text).

TABLE 4: COMPARISON OF CALCULATIONS AND OBSERVATIONS (MIXTURE B)

<u>Parameter^a</u>	<u>T/K</u>	<u>Observed</u>	<u>Set I^b</u>	<u>Set II^c</u>	<u>Set III^d</u>	<u>Set IV^e</u>	<u>Set V^f</u>
Flame band							
$t_{1/2}$	2085	17± 3	18	27	15	15	18
	2435	10± 3	12	--	--	--	--
	2840	7± 2	9	9	9	9	--
$t_{3/4}$	2085	25± 6	43	43	39	21	42
	2435	15± 5	17	--	--	--	--
	2840	8± 3	11	11	11	11	--
CO_2	2085	0.35±.05	0.32	0.30	0.33	0.37	0.32
	2435	1.20±.13	1.16	--	--	--	--
	2840	2.58±.26	2.82	2.75	2.89	3.01	--
$t_{.5}$	1875	60± 4	58	--	--	--	--
	2085	22± 4	24	21	27	33	24
	2435	8± 2	8	--	--	--	--
	2840	---	5	4	5	5	--
$t_{1.5}$	1875	115± 7	104	--	--	--	--
	2085	35± 6	41	38	45	51	43
	2435	14± 3	16	--	--	--	--
	2840	---	9	9	10	10	--
$t_{2.5}$	1875	160± 9	152	--	--	--	--
	2085	56± 7	61	58	65	72	64
	2435	26± 4	28	--	--	--	--
	2840	300±53	289	246	339	410	--

^aSee TABLE 1 for definitions.^bReactions 1 - 23 (TABLE 2)^c $k_{20} = 1.36 \times 10^{-9} \exp(-58.5 \text{ kJ/RT})$.^d $k_{20} = 3.4 \times 10^{-10} \exp(-58.5 \text{ kJ/RT})$.^e $k_{20} = 3.5 \times 10^{-11} \exp(-37.8 \text{ kJ/RT})$.^fIncluded additional CH₃ reactions (see text).

TABLE 5: COMPARISON OF CALCULATIONS AND OBSERVATIONS
 (235 ppm $(\text{CH}_3)_2\text{N}_2$, 4.18% CO, 2.13% O₂ in Argon)

<u>Parameter</u>	<u>T/K</u>	<u>Observed^a</u>	<u>Set A^b</u>	<u>Set B^c</u>	<u>Set C^d</u>	<u>Set D^e</u>
t_1^f	1500	300	180	215	128	270
	1750	110	110	115	80	160
	2150	60	64	65	45	90
α^g	1500	2	0.9	0.9	0.9	0.9
	1750	3	2.0	2.0	2.0	2.0
	2150	5	4.1	4.4	4.0	4.1

^aTaken from Figs. 2(a) and 3(a) of Reference 3.

^b"Standard Set"; see text.

^cIncluded CH₃ + CH₃; see text.

^d $k_{25} = 2.4 \times 10^{-12} \exp(-38 \text{ kJ/RT})$.

^e $k_{25} = 6.0 \times 10^{-13} \exp(-38 \text{ kJ/RT})$.

^fTime [CO₂] = $1.6 \times 10^{13}/\text{cm}^3$.

^gConstant (late) rate of CO₂ production.

LEGENDS

Fig. 1 Typical Flame-band Profiles. (a) Mixture A, $T = 2410K$. (b) Mixture B, $T = 2435K$. Open circles designate every fifth data point; closed circles are the calculated results. (Sets I and I.)

Fig. 2 Flame-band Parameters for Mixture A. (a) Time required to reach one-half maximum voltage. (b) Time required to reach three-fourths maximum voltage. (c) Maximum voltage. Open symbols are experiments, closed symbols are calculated values. (Set I.) All times are relative to t_0 . (See text.)

Fig. 3 Flame-band Parameters for Mixture B. Symbols have same meaning as in Fig. 2. Calculations are Set I.

Fig. 4 Typical CO_2 Profiles. (a) Mixture A, $T = 2410K$. (b) Mixture B, $T = 2435K$. Open circles are observed; closed circles are calculated. (Sets I and I.)

Fig. 5 CO_2 Parameters for Mixture A. (a) Time for $[\text{CO}_2]$ to reach $0.5 \times 10^{16}/\text{cm}^3$. (b) Time to reach $1.5 \times 10^{16}/\text{cm}^3$. (c) Time to reach $2.5 \times 10^{16}/\text{cm}^3$. Open symbols are observed; closed symbols are calculated. (Set I.) All times measured relative to t_{mp} . (See text.)

Fig. 6 CO_2 Parameters for Mixture B. Symbols have same meaning as in Fig. 5. Calculations are Set I.

FIG. 1

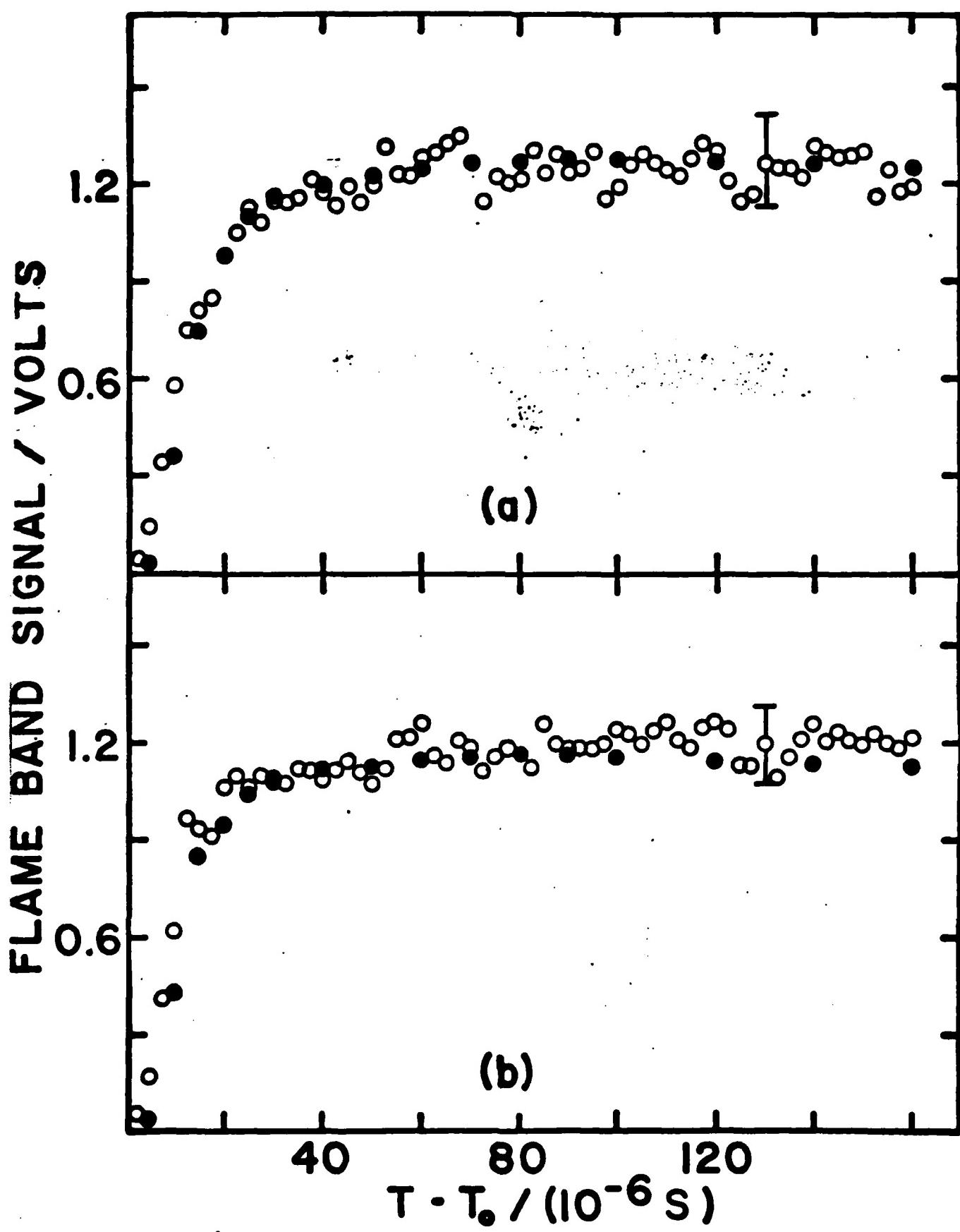


FIG. 2

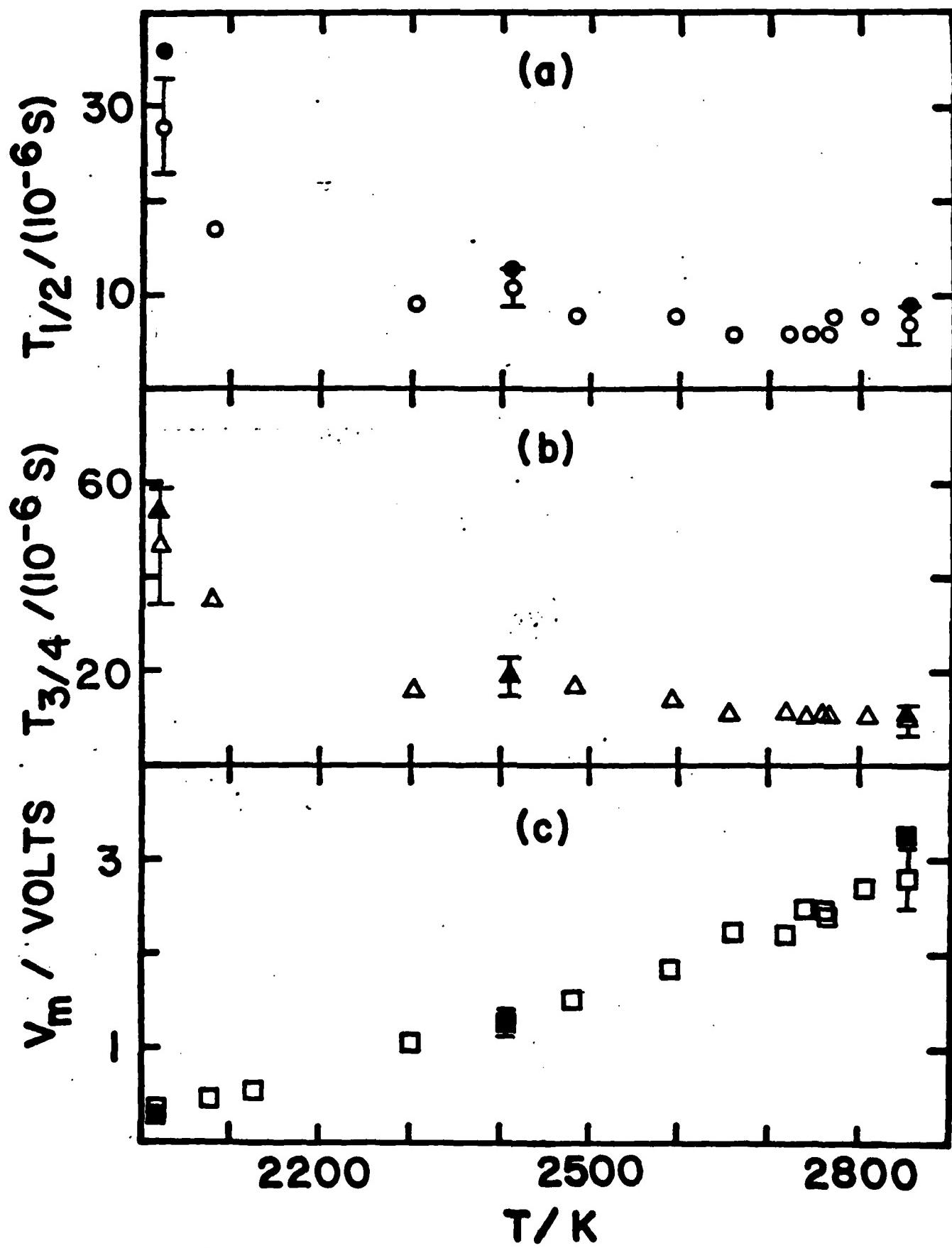


FIG. 3

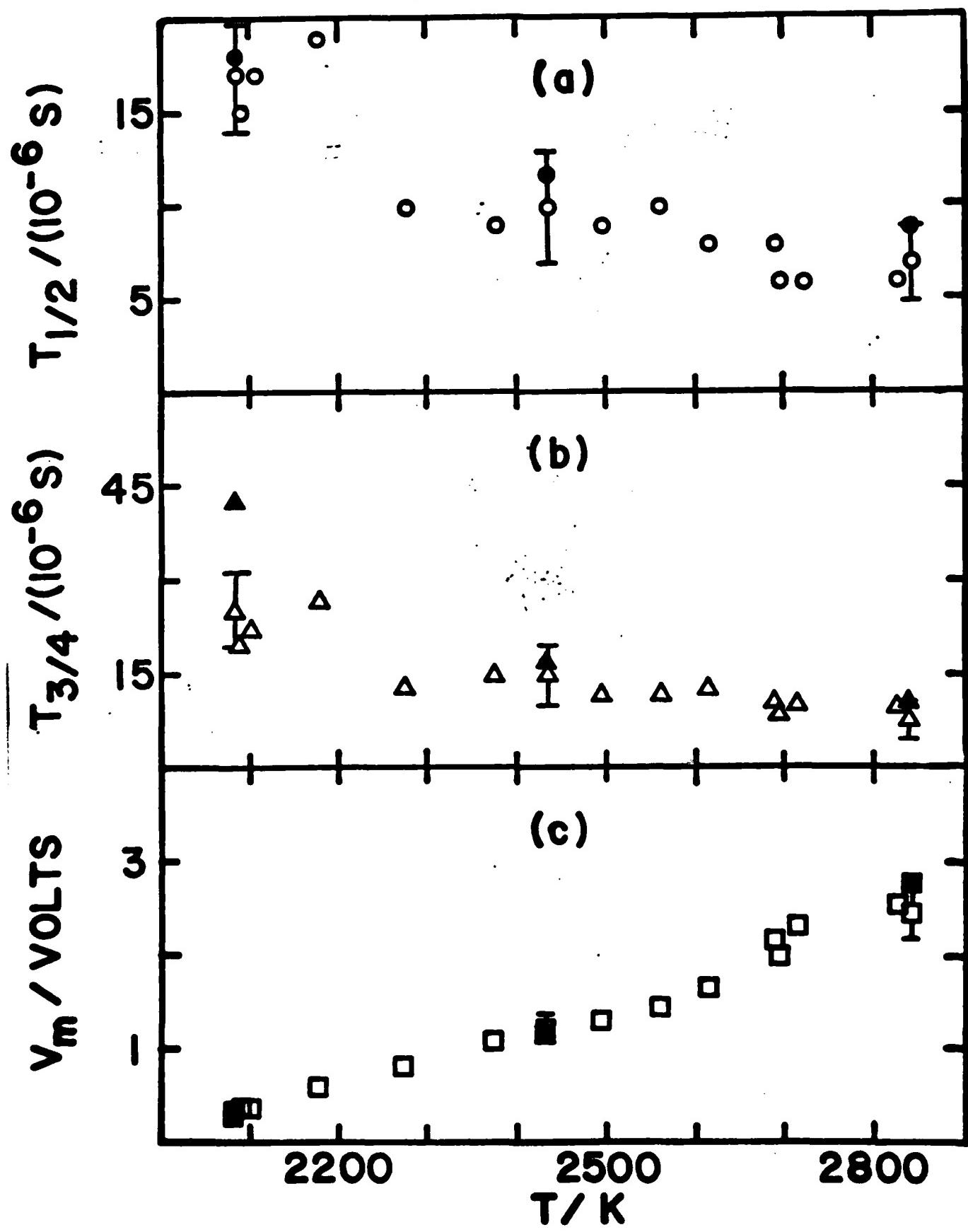


FIG. 4

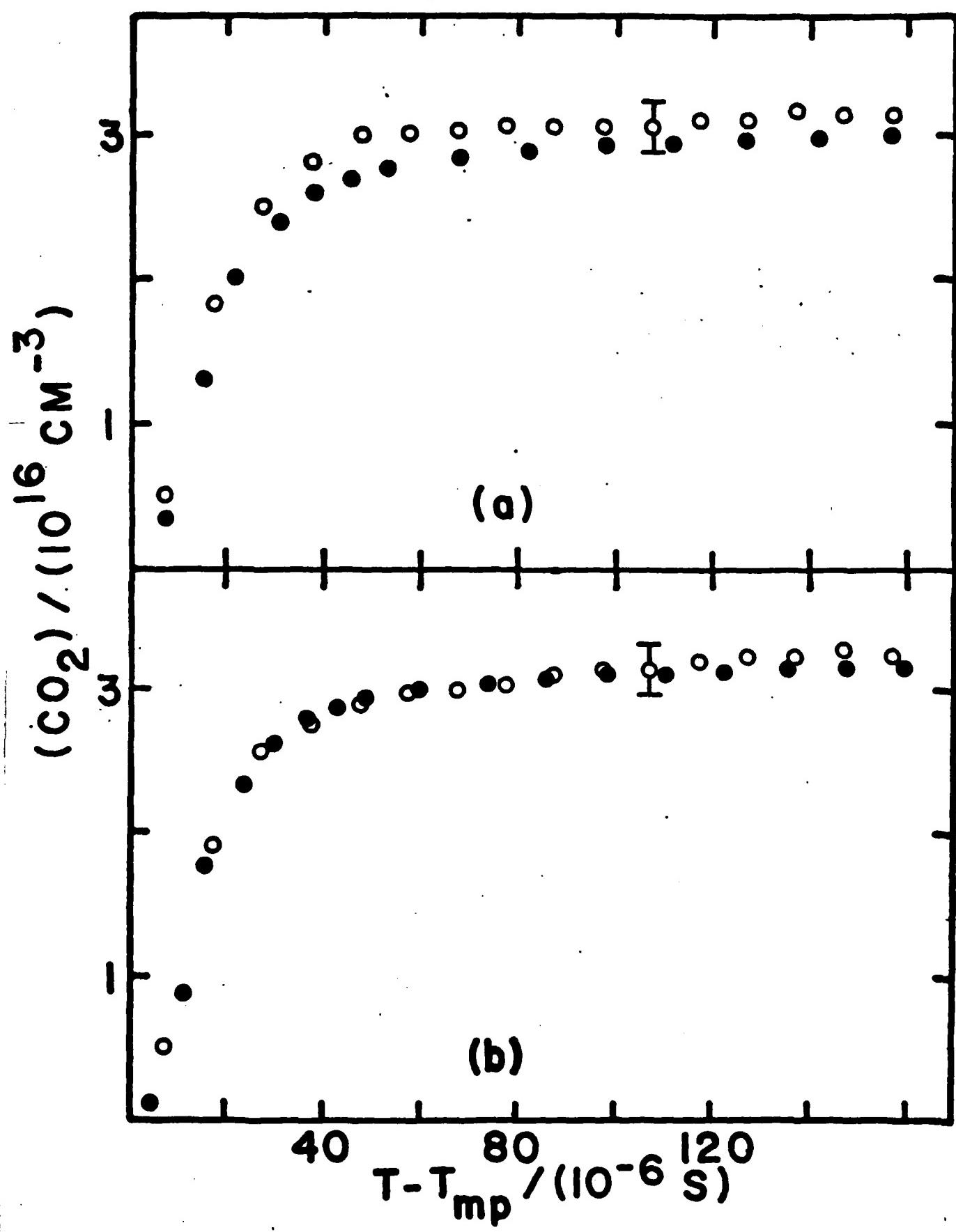


FIG. 5

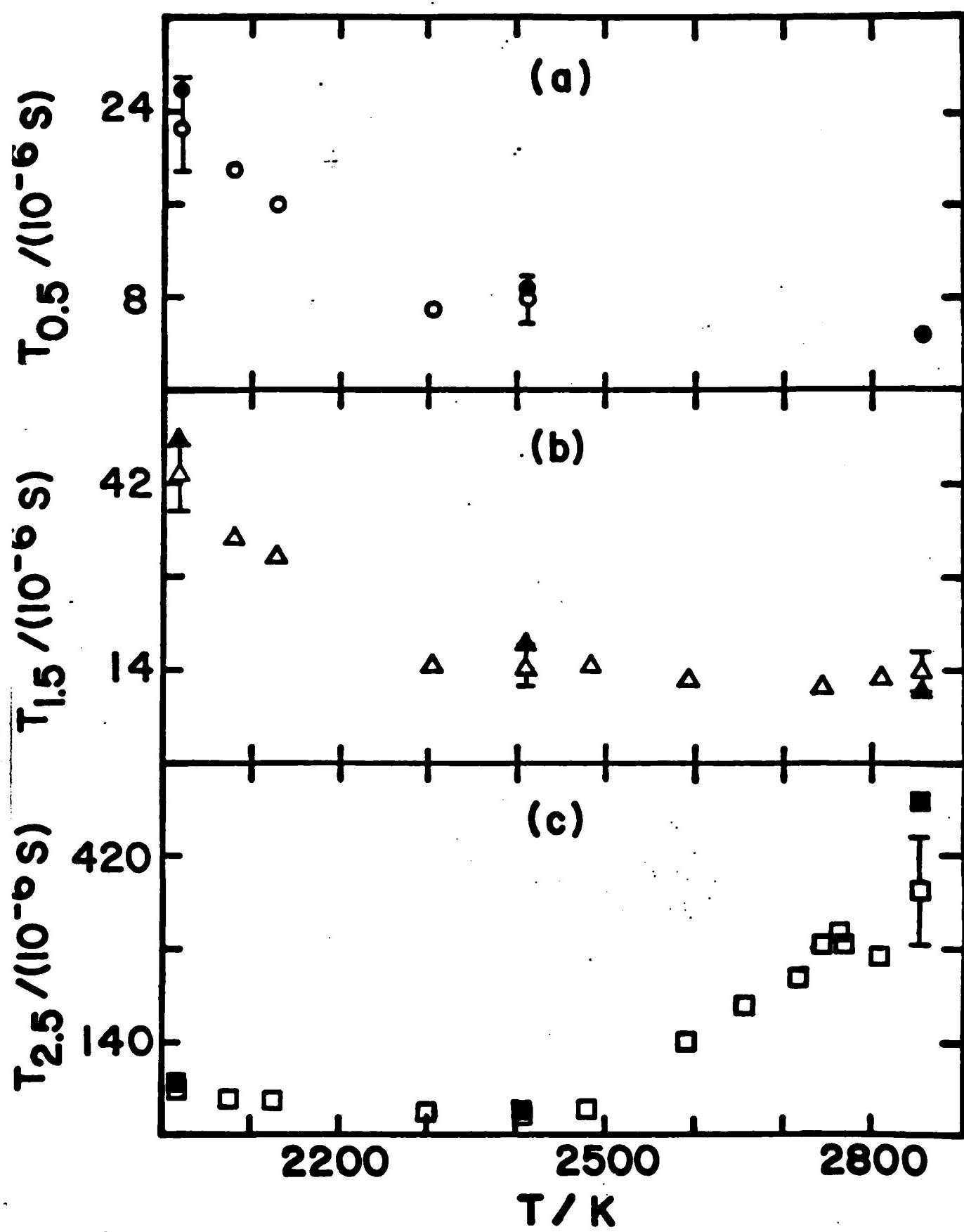
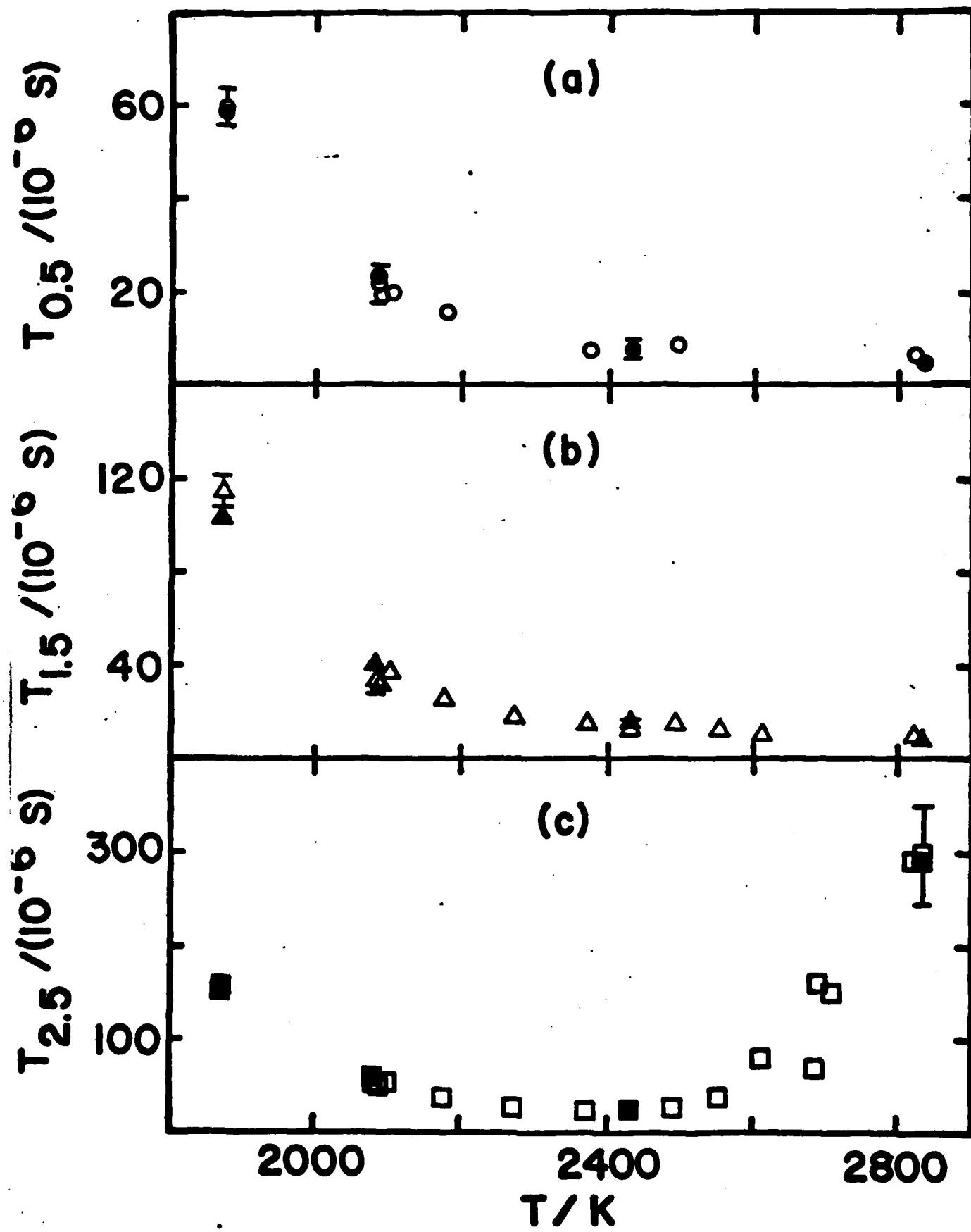
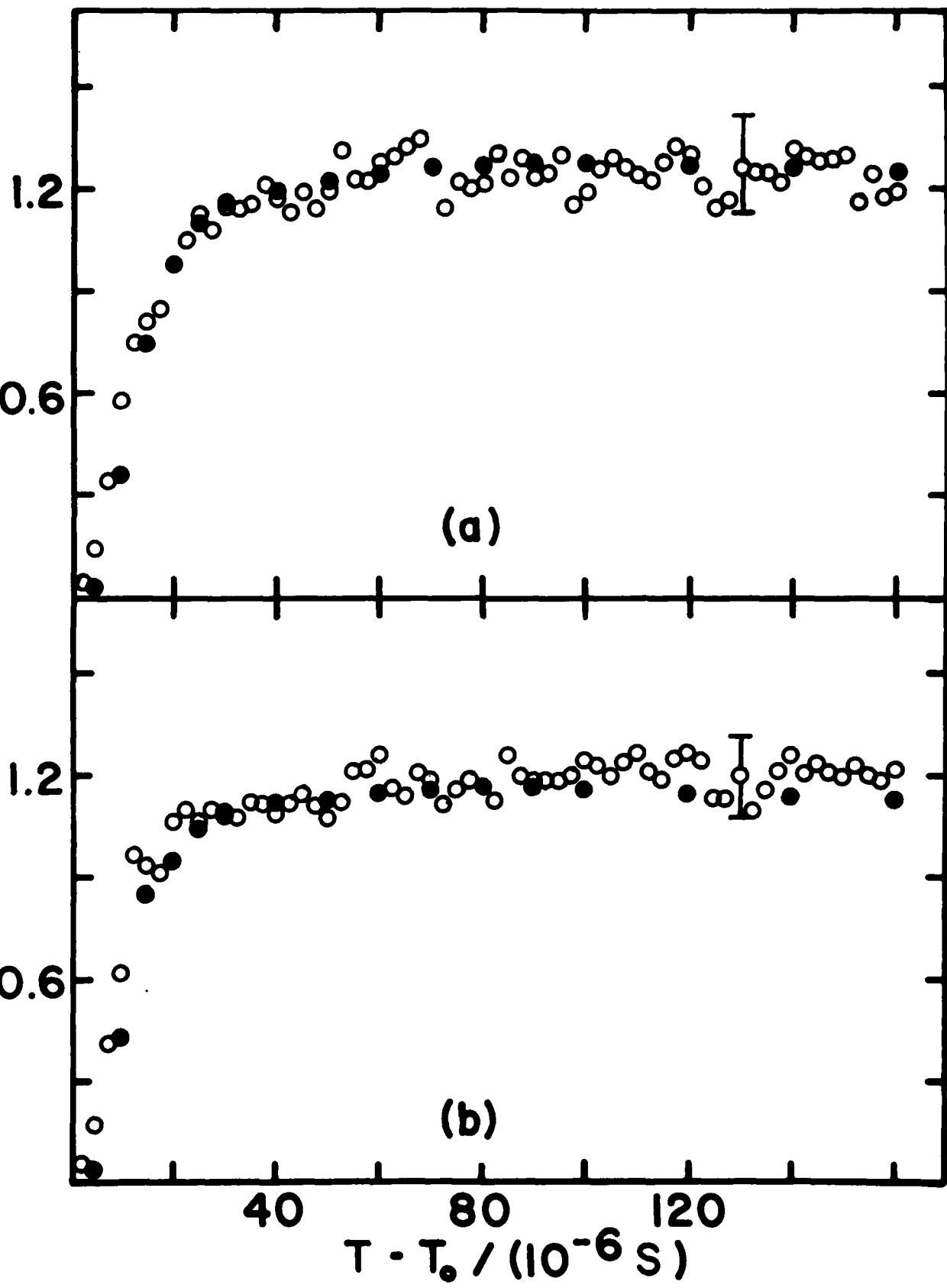
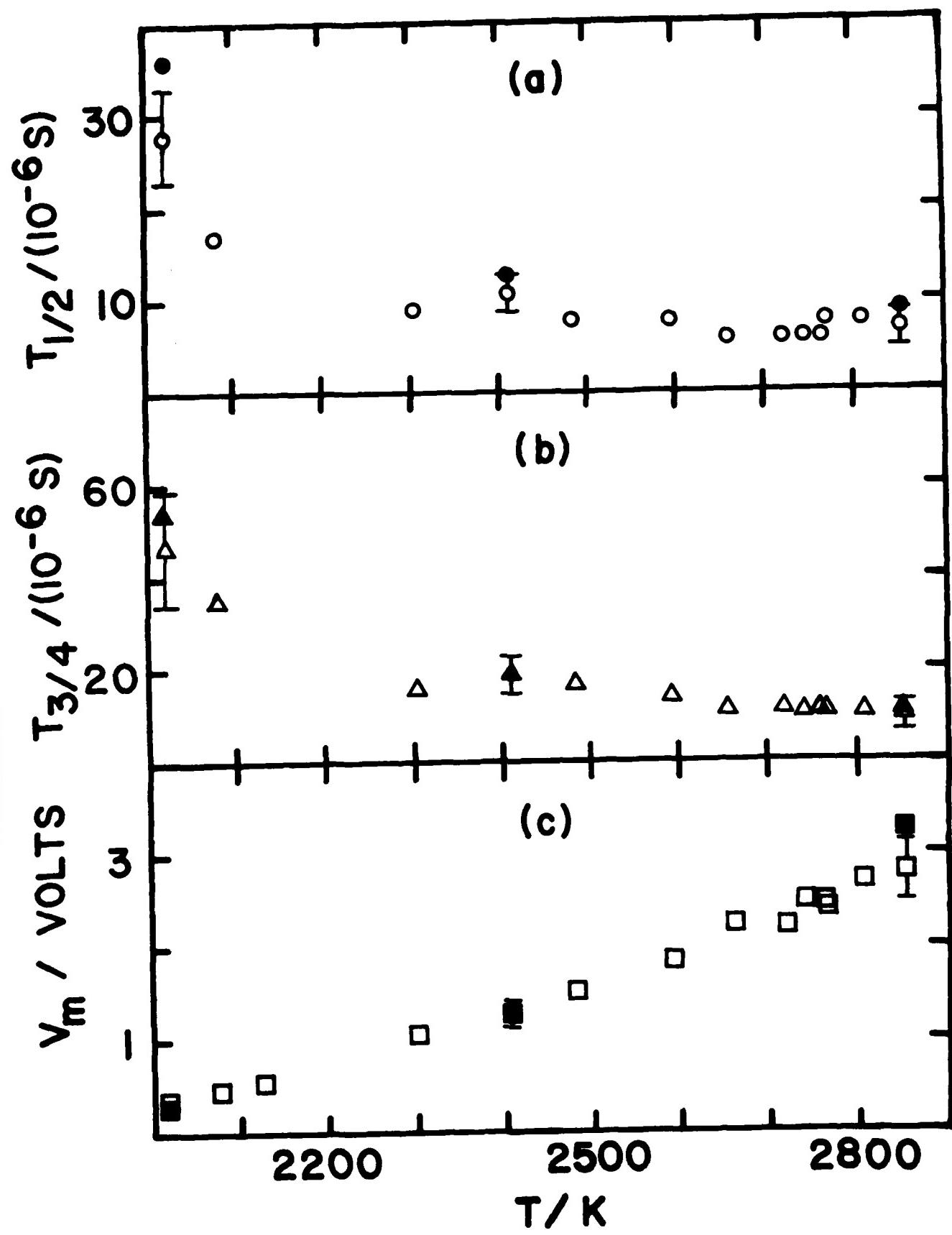


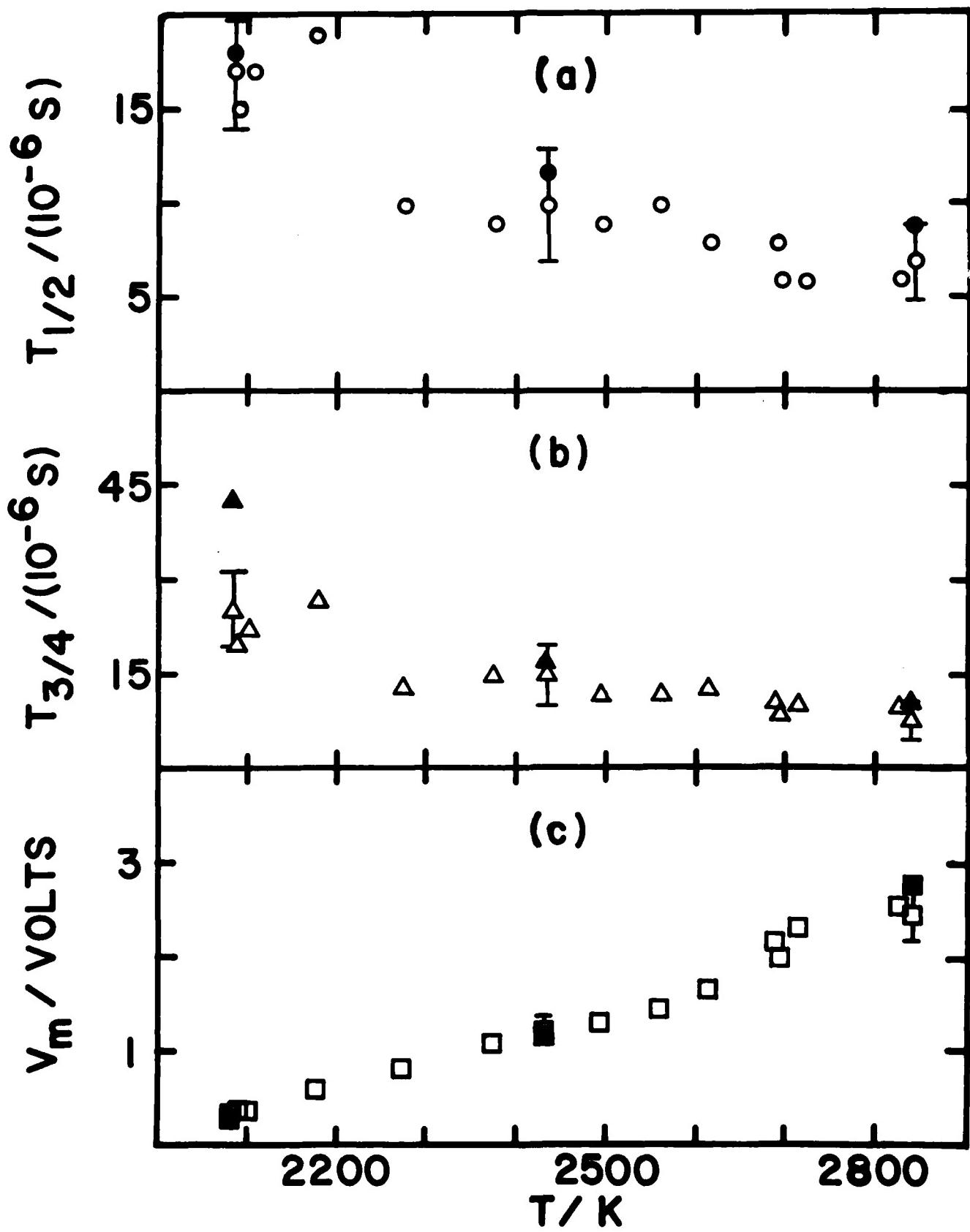
FIG. 6

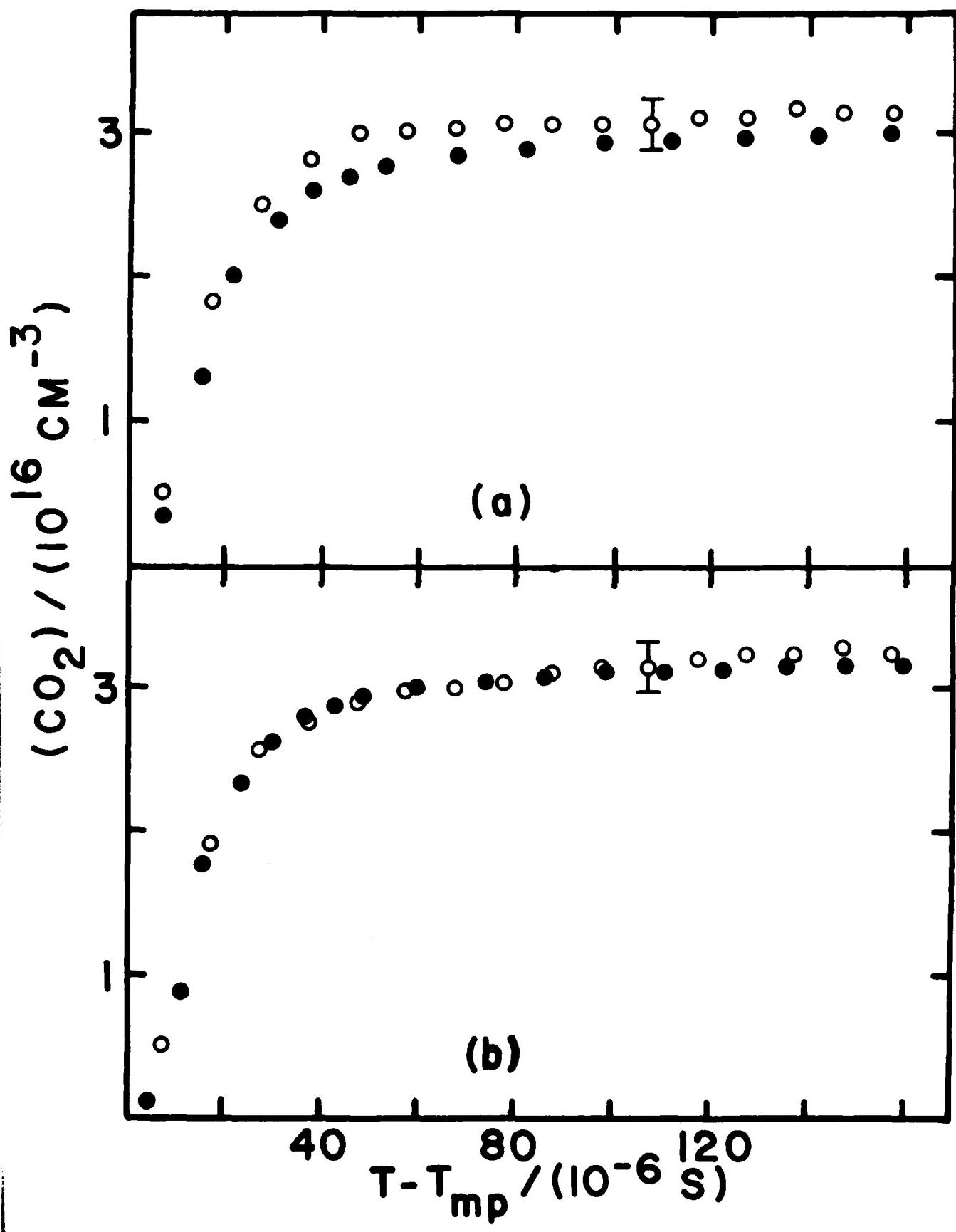


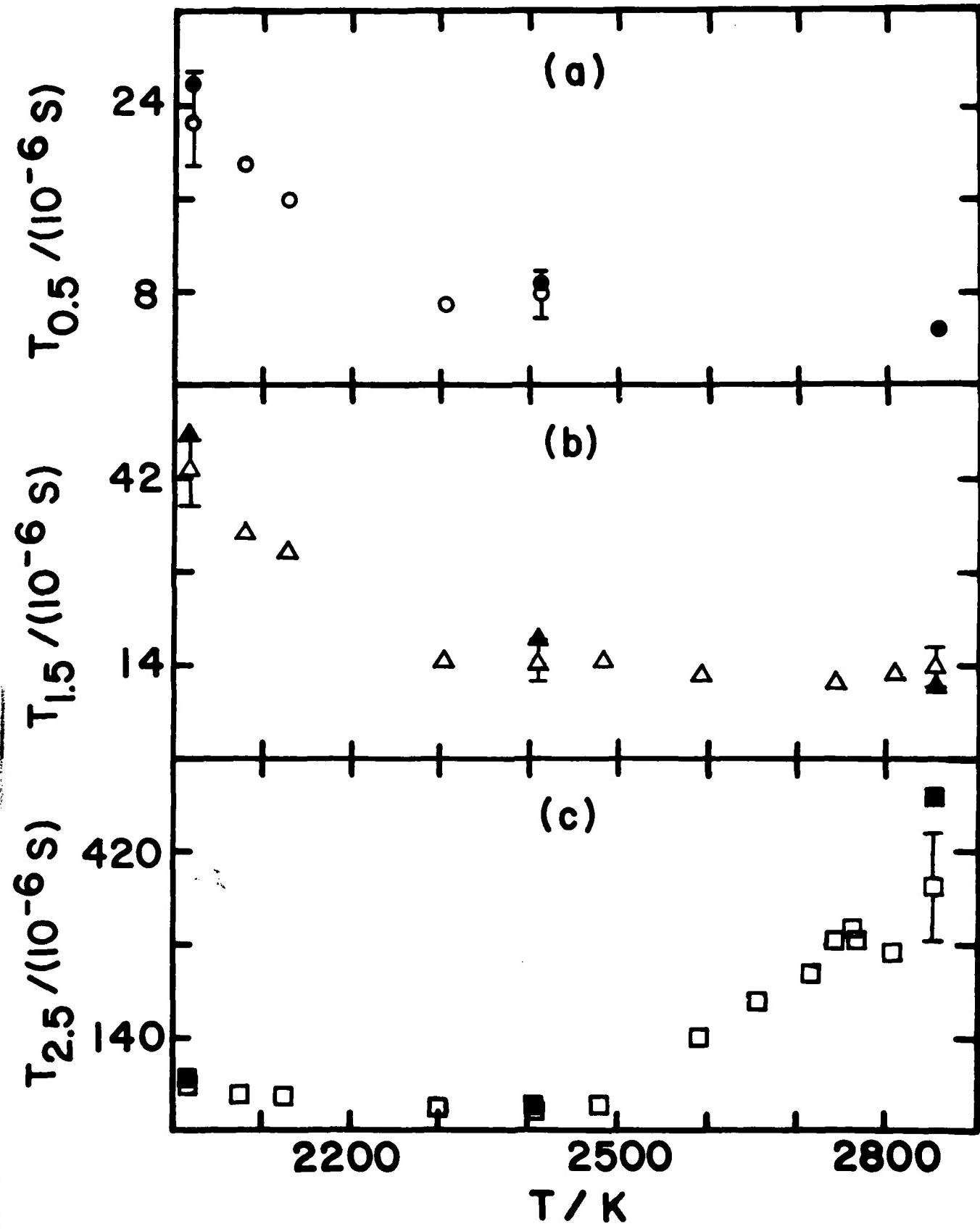
FLAME BAND SIGNAL / VOLTS

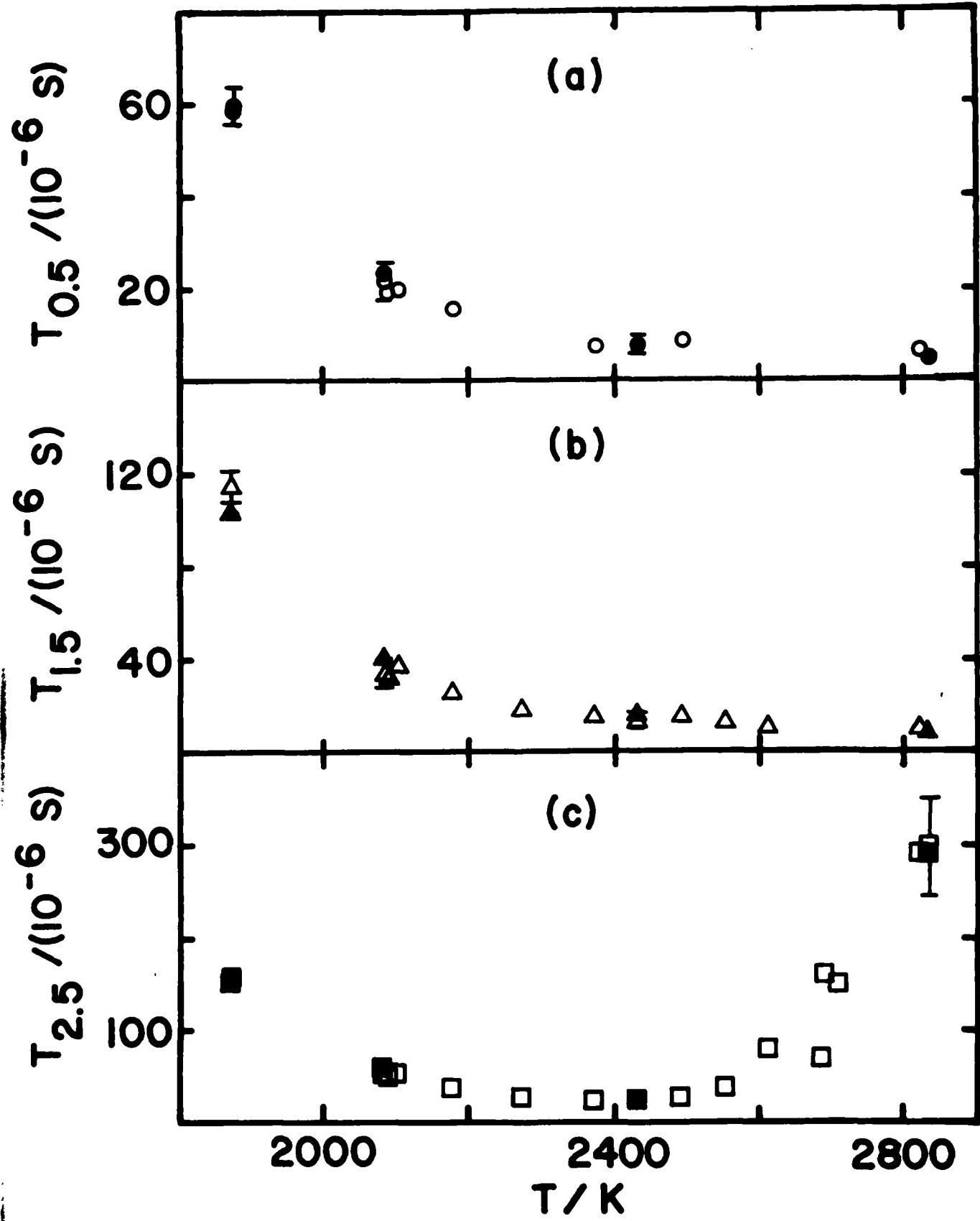












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4. TITLE (and Subtitle) <i>SHOCK TUBE STUDIES OF THE N₂O/CH₄/CO/Ar AND N₂O/C₂H₆/CO/Ar SYSTEMS.</i>	5. TYPE OF REPORT & PERIOD COVERED	
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19. KEY WORDS (Continue on reverse side if necessary and identify by block number) <i>Shock Tube studies Methane chemistry Formaldehyde chemistry Combustion</i>		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) <i>Reflected shock waves were used to heat N₂O/O₂H₆/CO/Ar and N₂O/CH₄/CO/Ar mixtures to temperatures of 1875-2855 K at total concentrations of 5 x 10¹⁸ cm⁻³. Oxygen atom production was monitored via the flame band emission at 450 nm, and CO₂ production was observed at 4.27 μm. These data were then compared to the results of numerical integration of the rate equations, using rate constant and mechanistic information obtained in earlier studies of H₂ and CH₄ under similar conditions. For the C₂H₆ mixture, it was possible to achieve good agreement between these calculations and the observed data using only one</i>		

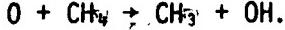
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additional reaction

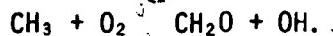


The calculations were insensitive to the precise value used, but the results are consistent with recent high temperature literature values. For the CH₄ mixture, the best agreement was achieved using a recent high temperature value for



The data indicated that this reaction has a markedly non-Arrhenius rate constant; use of a value based upon low temperature data gives results inconsistent with those observed. The CH₄ system was insensitive to any other methane reaction rate constant. There was some experimental evidence to suggest an unsuspected complexity in methyl radical decay channels at the lowest temperatures observed.

The mechanism/rate constant combination used here was then applied to the analysis of literature data for CH₃ oxidation by O₂. This analysis was designed to obtain a value for the rate constant of



Results indicated that the most recent high temperature studies yield values consistent with the present analysis.

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